PLEASE DO NOT REMOVE FROM LIBRARY

Bureau of Mines Report of Investigations/1985

Influence of Chelating Reagents on Leaching of Copper Ore

By Larry A. Haas and Terry L. Hebble





Influence of Chelating Reagents on Leaching of Copper Ore

By Larry A. Haas and Terry L. Hebble



UNITED STATES DEPARTMENT OF THE INTERIOR Donald Paul Hodel, Secretary

BUREAU OF MINESRobert C. Horton, Director

Library of Congress Cataloging in Publication Data:

Haas, L. A. (Larry A.)

Influence of chelating reagents on leaching of copper ore.

(Report of investigations; 8965)

Bibliography: p. 11-12.

Supt. of Docs. no.: I 28.23:8965.

1. Copper-Metallurgy. 2. Leaching. 3. Chelates. I. Hebble, T. L. (Terry L.), II. Title. III. Series: Report of investigations (United States. Bureau of Mines); 8965.

TN23.U43 [TN780] 622s [669.3] 85-600013

CONTENTS

		Page
Intr Ge Re Mate Expe In Ag Co Disc Conc	coduction. concerned background. crials. crimental results. cr	1 2 2 3 3 4 4 4 8 10 10 11 11
кете	rences	11
	ILLUSTRATIONS	
1. 2.	Influence of pH on iron and molybdenum concentration	4
3.	solubility Influence of pH and sodium lignin sulfonate concentration on iron and	5
4. 5.	molybdenum solubility	5 6
6.	5 g/L gluconic acid	6 7
7. 8.	Influence of pH and citric acid on titanium, molybdenum, and iron solubility	7
	dump leach ions	8
9.	Influence of agitation time and citric acid on leaching of ore A	9
10. 11.	Influence of agitation time and citric acid on leaching of ore B Influence of column leach time and citric acid on solution analyses and	9
	percolation flow	10
	TABLES	
1. 2.	Partial chemical analyses of ores	3 4

	UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT					
cm	centimeter	L/(m ² ·s)	liter per square meter per second			
ft	foot		mud in cata a			
ft ²	square foot	min	minute			
	-	mL	milliliter			
g	gram	mL/min	milliliter per minut			
gal	gallon		•			
ga1/(d•ft ²)	gallon per day	μm	micrometer			
	per square foot	m/s	meter per second			
g/L	gram per liter	pct	percent			
h	hour	ppm	part per million			
in	inch	tpy	ton per year			
kg	kilogram	yr	year			
L	liter					

*

INFLUENCE OF CHELATING REAGENTS ON LEACHING OF COPPER ORE

By Larry A. Haas 1 and Terry L. Hebble 2

ABSTRACT

A major problem encountered in dump leaching operations is the plugging of both the dump and the piping by precipitated iron compounds. Bureau of Mines research to obtain basic data on agitation leaching and dump leaching methods has shown that the addition of organic chelating reagents can significantly enhance the lixiviant permeability through the ore and the concentration of the metal values in the liquor. example, the addition of 5 g/L citric acid (CA) to a conventional sulfuric acid lixiviant almost doubled the fluid flow rate through 5-cmdiameter laboratory columns containing copper ore. After 185 h of percolation leaching, the metal concentrations with (and without, in parentheses) CA were 1.7 (1.5) g/L Cu, 200 (70) ppm Mn, 160 (40) ppm Al, and 6 (3) ppm Co. The enhancement of metal concentrations with chelating reagents such as CA was confirmed by determining the solubility of several metal ions as functions of pH and chelating reagent concentration. When ferric ions became insoluble at pH values above 3, the concentrations of other ions also decreased. The addition of chelating reagents kept iron, as well as the other dissolved metals, in solution even at pH values as high as 5. Citric acid was a more effective chelating reagent than gluconic acid, oxalic acid, or sodium lignin sulfonate.

¹ Research chemist.

²Metallurgist.

Twin Cities Research Center, Bureau of Mines, Minneapolis, MN.

INTRODUCTION

GENERAL BACKGROUND

The Bureau of Mines has investigated various hydrometallurgical methods for extracting copper and other metal byproducts from domestic low-grade copper materials. Each year, several million tons of copper wastes are added to the existing accumulation of over 4 billion tons (3). The distribution ratios of metal byproducts to copper in the low-grade materials are somewhat similar to those in the high-grade copper ores. third of the total molybdenum, silver, and gold produced in the United States is obtained from high-grade ore, but only copper and a small quantity of uranium are recovered from low-grade waste rock. Currently, copper leached from dumps accounts for about 15 pct of the total copper production. Wyoming Minerals, Inc., has been producing about 70 tpy of uranium from the Kennecott Bingham Canyon copper dump liquor (about 5 ppm U₃O₈) (4). Even though U_3O_8 concentration is low, considerable amounts are produced of liquor because large volumes treated. Bieniewski (2) estimated that about 30,000 tons of $U_{3}\overline{O}_{8}$ could be recovered during the next 30 yr from copper dump liquors containing 1 to 12 ppm U₃O₈.

The concentrations of several of the refractory metals such as titanium and molybdenum are extremely low (less than 1 ppm) in the liquors from acid leaching operations. Previous work in this laboratory has shown that one reason why molybdenum concentrations in leach liquors are low is that the molybdenum is removed with the iron precipitate as it forms in the dump.

Not only does iron precipitation remove metal values from solution, it also causes a decrease in the rate of flow of liquids and gases through the dump, which increases the cost of the operation. In commercial operations, pipelines that are constricted by the precipitated iron salts are opened with mechanical devices,

but clearing of most of the flow channels inside a dump is conceivable only by chemical means. Periodically breaking up the surface by digging furrows or scraping the surface and dumping the rusty material over the edge of the dump are means by which the permeability of dumps is improved (10).

Other methods of increasing the dump permeability are drilling vertical holes into the dump and casing the holes with perforated plastic pipe, and oxygen injection. However, these methods only briefly increased the liquid flow rate in a laboratory column (6). Sulfur dioxide has also been tried to unplug a column, but it only temporarily increased the flow. For example, treatment of a 773day-old leaching column with sulfur dioxide increased the percolation rate from 2.4 to 94.7 $gal/(d \cdot ft^2)$ (1.8 to 70.7 $\times 10^{-2} L/(m^2 \cdot s)$, but at 31 days after the treatment, the rate decreased to 13.6 $ga1/(d \cdot ft^2)$ (10.2 × 10⁻² L/m²·s)) (7). In some operations, solvent extraction rather than scrap iron cementation is being implemented for the recovery of cop-This innovation eliminates the exposure of the aqueous solution to scrap iron and results in a substantial reduction of iron in the dump leach solution. However, the iron dissolved from the dump ore itself is still enough to cause iron precipitation problems.

It is well known that increasing the acidity of a leaching dump will improve its permeability and remove some of the iron salts deposited in the plumbing components of the operation. However, the pH would have to be decreased to about 1, and at this pH, rapid corrosion of the metal piping occurs. The proposed use of chelating reagents as additives to prevent iron salt precipitation does require a change in pH. As such, present operating cost of dump leaching probably would be reduced because (1) the life expectancy of the metal plumbing components would be extended and (2) the dumps would not have to be "ripped" as Also, it should be possible to make the dump leach pads deeper because plugging would be less severe.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The use of chelating reagents to stabilize metal ions in solutions is not new. Many industrial processes contain unwanted metal ions which must be chelated to keep them in solution. Chelating reagents securely bind some metals to form stable ions, which are usually water soluble and are quite resistant to the action of oxidizing or reducing reagents. The food, soap, and detergent industry uses a large quantity of chelating reagents. Also, water is commonly softened by chemical treatment using inorganic polyphosphates since they are relatively cheap. Polyphosphates prevent the formation of precipitates in hard water containing calcium and magnesium. Recently, organic chelating reagents (alkali metal salts of the hydrology acids and the aminopolycarboxylic acids) such as ethylenediaminetetra acetic acid (EDTA) and 2-hydroxy-1, 2, 3-propanetricarboxylic acid (citric acid or CA) have become increasingly important.

Some chelates, such as EDTA, stabilize the calcium ions to prevent the formation of water-insoluble calcium precipitates. Other common dump leaching ions (such as silver, cobalt, nickel, manganese, magnesium, uranium, aluminum, and zinc) can form water-soluble chelates and thereby

permit a higher concentration of these metals in solution before their solubility limit is exceeded. The chelate, citric acid, was chosen for most of the experiments in this study. This chelate was used previously in a different large-scale metallurgical application (8).

RESEARCH PLAN

The goal of this research was to determine if the addition of chelating reagents to simulated dump leaching lixiviants could increase the dissolution of metals and the liquid flow rates. research was divided into three phases. In phase 1, an assortment of synthetic copper dump lixiviants (with and without chelating reagents, molybdenum, titanium, etc.) were prepared, and their pH's were adjusted by the addition of various neutralizers. These solutions were used in agitation and percolation leach tests to determine the influence of pH and chelating reagents on metal solubility. In phases 2 and 3, the neutralized lixiviants' capabilities to extract copper and byproduct metals from a copper ore by agitation leaching and percolation leaching, respectively, were compared.

MATERIALS

The solutions used in this research were prepared from reagent-grade metal sulfate salts. Copper ores A and B, obtained from two copper mining companies in the Western United States, were used. Partial chemical analyses of the ores are shown in table 1. Petrographic analyses

Not determined.

indicated that ore A (low-grade copper ore) contained quartz, microcline, plagioclase, mica, chalcopyrite, bornite, covellite, pyrite, rutile, and molybdenite,
and ore B (high-grade copper ore) contained quartz, feldspar, mica, clays, amphiboles, hematite, goethite, rutile,

TABLE 1. - Partial chemical analyses of ores, weight percent

Specie	Ore A	Ore B	Specie	Ore A	Ore B
Fe	2.2	4.8	Mo	0.025	0.029
A1	6.3	5.0	Na	•05	.04
Ca	1.3	4.1	Ni	.02	.02
Co	.02	.02	S	•3	.04
Cr	ND	.02	Si	28.6	29.9
Cu	.23	1.6	Ti	•32	.31
K	•52	1.3	Zn	.005	.086
Mg	2.6	9.6	CO3	•5	•5
Mn		.47			

and cuprite. Grinding of the ores to different sizes was done with jaw crushers and pulverizers. Ore A was ground to 100 pct minus 100 mesh, and ore B to 100 pct minus 2 mesh (table 2).

EXPERIMENTAL RESULTS

INFLUENCE OF PH AND CHELATING REAGENTS ON METAL ION SOLUBILITIES (PHASE 1)

A main byproduct of processing copperrich ores is molybdenum; therefore, in phase 1, tests were conducted initially with solutions containing only this metal Sodium molybdate (Na2MoO4 • 2H2O) was dissolved in distilled water to make a solution containing about 0.2 g/L Mo. The acidity of 0.5 L of this solution was adjusted first to a pH of l with concentrated sulfuric acid and then to a pH of 10 with 60-pct-NaOH solution. Essentially no change in molybdenum concentration was observed when the pH adjustments from 1 to 10 were made with sulfuric acid and NaOH solutions. However, when ferric sulfate (about 1.5 g/L Fe)4 was added to the acidified molybdenum solution, the pH

⁴Wherever Fe is used in the remainder of this report, it implies that the iron is in the ferric oxidation state.

TABLE 2. - Size distribution of sample charge and leached discharge of ore B, percent

Par	rticle	size	Charge	Dis-	
					charge 1
Minus	9.52	plus	6.68	14	12
Minus	6.68	plus	3.33	24	25
Minus	3.33	plus	1.65	10	10
Minus	1.65	p1us	0.83	8	8
Minus	0.83	plus	0.59	12	12
Minus	0.59	p1us	0.29	5	4
Minus	0.29	plus	0.15	7	6
Minus	0.15	plus	0.074	20	8
Minus	0.074	plus	0.038	0	. 15
7	otal			100	100

The discharge values refer to the average screen size analyses after the ore was percolation-leached for 350 h in a glass column as described in the phase 3 experiment without CA added. The size distributions with and without CA were essentially the same.

increased from about 1 to about 7, and a sharp drop in the iron and molybdenum concentration occurred at about pH 3 (fig. 1). Essentially the same iron concentration decrease was obtained with a different solution containing only iron and no molybdenum. The vertical bars in figure 1 depict the range of the analyses

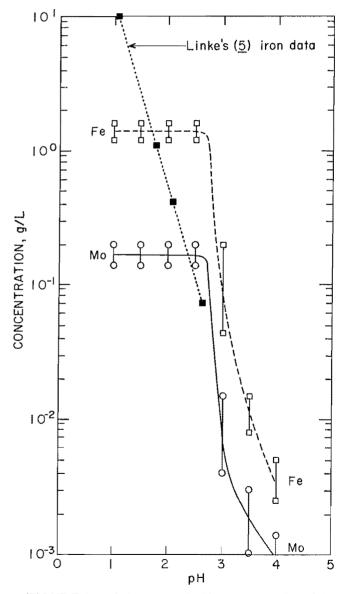


FIGURE 1. - Influence of pH on iron and molybdenum concentration.

when different neutralizers in water, such as NaOH (60 pct), CaCO₃ (100 pct), and NH₄OH (28 pct), were used. After the pH values of the solutions were adjusted and allowed to set for 30 min, the solutions were passed through a 0.45-µm poor filter. A few drops of concentrated sulfuric acid were added to the 50-mL aliquots of the filtrates to decrease the pH to less than 1, which prevented further precipitation during the chemical analyses operation. When a sample at a pH of 2.8 was allowed to set for 100 h, essentially no decrease in metal concentration was obtained; in 300 h, over 40 pct of the iron and molybdenum were precipitated from the solution. These results illustrate why Linke's (5) iron solubilities in figure 1 were lower than the results obtained in this investigation. His results were obtained at equilibrium with a pure system, whereas the Bureau's were not. Randolph (9) also reported that the hydrolysis of ferric sulfate is slow but speeds up if hematite nucleation sites are made available.

Sodium hydroxide was used as the neufor the tralizer remaining titration studies. The chelating reagents added to the iron-molybdenum solution were 8 g/L trisodium N-hydroethylenediaminetriacetic acid (NazHEDTA) or 10 g/L sodium lignin sulfonate (SLS). With these additives, decrease in the iron or molybdenum concentration was detected even at a pH of 5 (fig. 2). However, when the SLS concentration was decreased to 5 g/L, the iron and molybdenum concentrations in the solution started to drop at pH values greater than about 3 (fig. 3).

Lower levels of chelate were required when SLS was substituted by gluconic acid (GA). The results shown in figure 4 indicate that the threshold pH values at which the metal concentrations decrease are 2.7, 3.3, 3.9, and 4.6 with 0, 1.25, 2.5, and 5.0 g/L GA, respectively. With the 5-g/L-GA addition and at a pH of 6.1, over 90 pct of the iron and molybdenum remained in solution. However, when the iron concentration was increased from 1.3 to 4.3 g/L with a 5-g/L-GA liquor, the molybdenum and iron concentrations

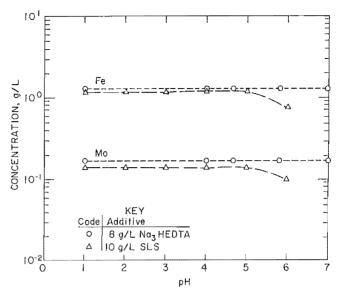


FIGURE 2. - Influence of pH and different chelating reagents on iron and molybdenum solubility.

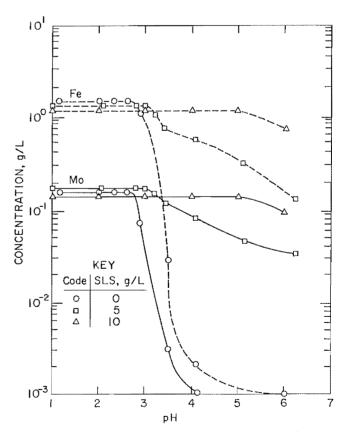


FIGURE 3. - Influence of pH and sodium lignin sulfonate concentration on iron and molybdenum solubility.

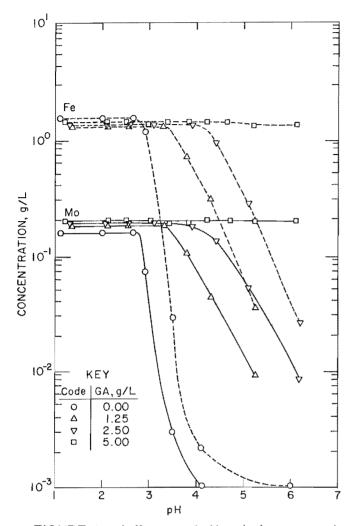


FIGURE 4. - Influence of pH and gluconic acid on iron and molybdenum solubility.

started to decrease at pH values above 2.9 (fig. 5). These results indicate that the threshold pH for preventing the decrease of the concentration of the metal ions depends on both the chelate and iron concentrations.

Other complementary tests were studied to determine the effects of chelating reagents on the solubility of other ions such as copper and titanium. Figure 5 shows that the copper content did not decrease when the pH was increased to 6.1 with the 1.3-g/L-Fe, 0.2-g/L-Mo, and 5-g/L-GA solutions. But with a solution containing 4.3 g/L Fe, copper was removed at pH 3.9 even with 5 g/L GA present. In another test with a 1.3-g/L-Fe solution with no GA, the copper concentration started to drop at pH 3.5. These results

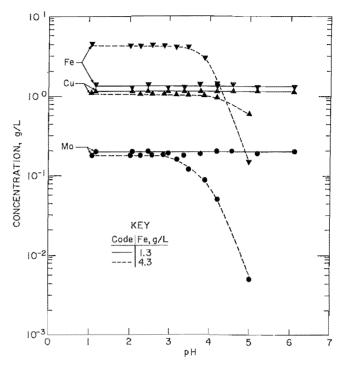


FIGURE 5. - Influence of pH and initial ferric concentration on metals solubility with 5 g/L aluconic acid.

indicate that a chelate is helpful in preventing the removal of copper, but if a large quantity of iron (4.3 g/L) is present, more than 5 g/L GA is necessary to prevent the copper removal at pH 3.9.

Titanium solubility, with and without chelating reagent, also was determined. When a titanium sulfate liquor (acidified with sulfuric acid) was neutralized with sodium hydroxide, the titanium concentration started to drop at a pH of about 1.5 with or without the presence of 1.2 g/L and 0.14 g/L Mo (fig. 6). However, when 1 g/L CA was added to the liquor, the titanium concentration did not drop until a pH of greater than 2.5 was reached. These results indicate that titanium is not coprecipitated with iron at pH levels below 2.5 but is hydrolyzed to form an insoluble compound if no chelating reagent is present.

With a different set of solutions, with or without molybdenum present, essentially the same titanium concentration-pH behavior was observed. With 2.5 g/L CA, essentially no drop in the titanium, molybdenum, or iron concentration was noted even at a pH of 5.5 (fig. 7).

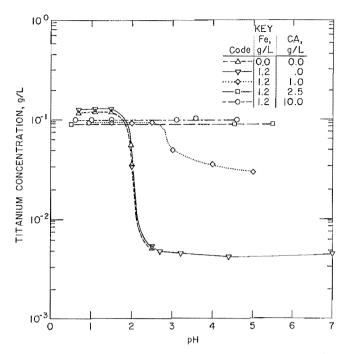


FIGURE 6. - Influence of pH, ferric ion, and citric acid on titanium solubility.

Oxalic acid (OA) was also used with a solution containing 0.09 g/L Ti, 0.14 g/L Mo, and 1.2 g/L Fe. The concentration of all three of these metals dropped at pH levels greater than 2.7, 3.0, and 6.0, with 1, 5, and 10 g/L OA, respectively. CA appears to be a more effective chelating reagent to keep these metals in the solution at a pH up to about 6 because four times more OA than CA was required.

Most dump leach solutions contain ions other than those already mentioned. other ions are Al, Mg, Mn, and Na, and their influence by chelating reagents has not been previously examined. Therefore, a simulated dump leach solution was prepared containing, in g/L, 5.8 A1, 0.93 Cu, 1.1 Fe, 2.2 K, 7.2 Mg, 0.78 Mn, 11.6 Na, and 0.15 Ti. No precipitate and essentially no decrease in metal ion concentration were observed until a pH of 3.5 was reached; thus the results are in agreement with those of previous investigators (1), who also reported that the pH required for precipitation of ferric ions can be increased by increasing the metal sulfate concentration. Also, no decrease in metal ion concentration was observed at a pH of 4.5 when 10 g/L

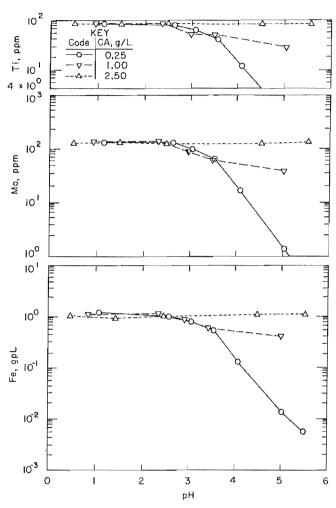


FIGURE 7. - Influence of pH and citric acid on titanium, molybdenum, and iron solubility.

of either SLS, disodiumethylenediaminetetracetic acid (Na₂EDTA·2H₂O), or potassium tartrate was added to the liquor. These chelating reagents prevented the precipitation of ferric ions even when several other metal sulfates were present.

CA (10 g/L) was used with a different simulated dump leach solution containing, in g/L, 0.04 Ti, 0.07 Ni, 0.1 Mo, 0.8 Cu, 0.05 Co, 0.25 Al, 1.0 Fe, 0.7 Mn, and 2.5 Mg. As the pH was increased to about 5, the only variation in metal concentration that was observed was mainly due to the dilution from the sodium hydroxide neutralizer. However, when these CA solutions were allowed to stand for several weeks, a scum was noticed. When 0.1 g/L potassium sorbate (KB) was added

internally to the CA-containing solutions, no scum was observed in solutions that were 1 yr old. The chelating effectiveness of 10 g/L KB alone was then determined, but it was found to be much less effective than CA or Na₂EDTA·2H₂O (fig. 8). Also, the addition of 0.1 g/L KB to the 10-g/L-CA solution did not change the effectiveness of CA, but it did stop the scum from forming.

To evaluate the recyclability of the chelating reagents such as would be required in copper cementation operations, another test was conducted with the simulated dump solution with 10 g/L Na₂EDTA, only with most of the copper removed by

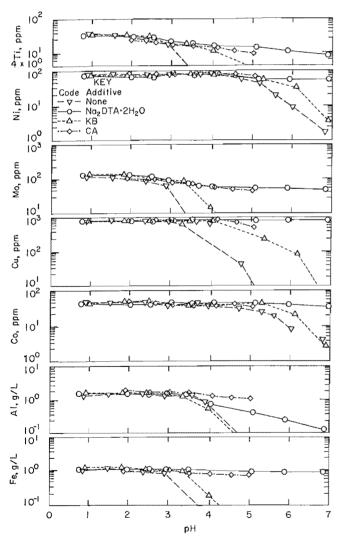


FIGURE 8. - Influence of pH and chelating reagents (10 g/L) on concentration of common dump leach ions.

treating 1 L of the solution with 1.5 g each of powdered iron and nickel for 12 h. This treatment dropped the copper content from 0.93 to 0.008 g/L. The pH of the decopperized solution was then increased with sodium hydroxide. Again a pH of about 4.5 was required before the iron was precipitated.

Another decopperizing experiment was conducted with a simulated dump solution containing 5 g/L CA. The solution was shaken for 1 min with an equal portion of 10-pct LIX 64N⁵ (manufactured by Henkel Corp.) dissolved in Napoleum 470 (a highflash-point kerosene obtained from Kerr McGee Oil Co.). This copper removal procedure was repeated four times with unloaded LIX 64N. The copper-depleted solution (0.1 g/L Cu) was then titrated with sodium hydroxide. Again, no precipitate or metal concentration decrease was obtained until a pH of about 4.5 was These results indicate that decopperizing the liquor did not destroy chelating reagent, and it appears that the chelating reagent may be recyclable.

AGITATION LEACH STUDIES (PHASE 2)

In phase 2, copper ores A and B were digested in an agitated reactor with various lixiviants. The principal lixiviant (L1) consisted of ferric sulfate (1 g/L Fe) and sulfuric acid (50 g/L). To half of the total lixiviant, 10 g/L CA was added to produce lixiviant (L2). Then 1.5-L portions of lixiviants Ll and L2 were added to two different 2.5-L jugs containing 500 g of ore A (100 pct minus 100 mesh). The air-vented jugs were agitated on a shaking table at 160 excursions (1/4 in or 6 mm) per minute.6 h of agitation, 50-mL aliquot slurry samples were taken. The filtrate analyses indicated that the pH values were 1 (fig. 9) and not 3 as anticipated. attain a pH value of 3, the ore charge was increased from 500 to 750 g, and agitation was extended from 6 to 24 h.

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

resulted in a slightly higher pH but less than 2, so another 500 g of ore was added to each jug. After a total of 48 h of leaching, the pH values of the solutions with and without CA were and 2.3, respectively, and the iron and titanium concentrations had dropped more than one order of magnitude in the solution without CA. Another 150 g of ore was added to the jug without CA, and 350 g was added to the jug with CA. After a total time of 72 h of leaching, the pH of the filtrates with and without CA had increased to 3.0 and 3.2, respectively. No further solid additions were made, but the agitation continued for 244 h. With this additional leaching time, the metal concentrations did not increase appreciably, but they were higher in the solution that contained CA.

Another series of agitated leach tests were conducted with only the coarse fraction (minus 3/8-in, plus 3 mesh; or minus

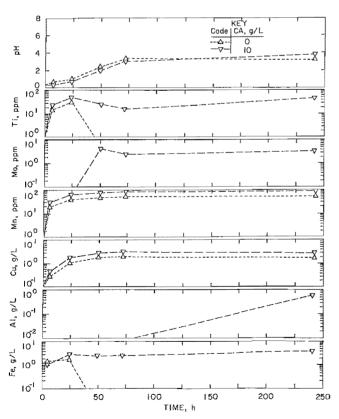


FIGURE 9. - Influence of agitation time and citric acid on leaching of ore A.

9.52, plus 6.68 mm) of ore B and with two different lixiviants. Both lixiviants contained ferric sulfate (1 g/L Fe). one also contained 5 g/L CA. The pH of both lixiviants was adjusted to 1.8 with concentrated sulfuric acid. One and onehalf liters of each lixiviant was added separately to the two jugs containing 1.5 kg ore. It is evident from the filtrate analyses that the dissolved metal content of the liquor was always higher with the solution that contained CA (fig. 10). Without CA present, the iron, aluminum, and copper concentrations dropped at pH values above 3. The metal concentration with CA was enhancement greater the coarser ore B (fig. 10) than with the finer ore A (fig. 9). These results

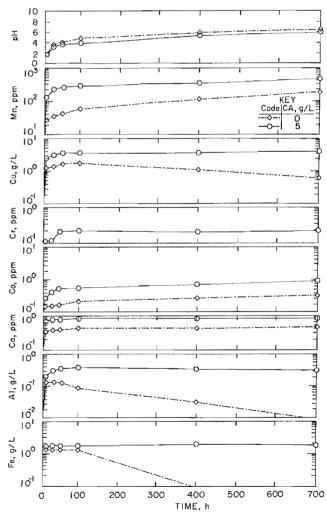


FIGURE 10. - Influence of agitation time and citric acid on leaching of ore B.

suggest that mass transfer may be an important leaching variable and that CA may prevent the plugging of intraparticle pores in the large particles.

COLUMN LEACHING TESTS (PHASE 3)

In the phase 3 studies, two glass burettes (5-cm diameter by 60 cm long) were each filled with 1.5 kg of ore B. Thirty liters of ferric sulfate solution (1 g/L Fe) were prepared, and 5 g/L CA was added to half of the total volume. Then the pH of both halves was adjusted to 1.6 with concentrated sulfuric acid, and both were placed in 20-L carboys above the columns at a height to produce a hydrostatic head of 30 cm. The lixiviants were allowed to percolate through the ore columns, and a 50-mL portion of the effluent was periodically analyzed. The remaining effluent was recycled with a diaphragm pump to the carboys. It is evident from the effluent analyses (fig. 11) that the pH reached a high level in the first 15 h because the ore was consuming acid. However, as more solution passed through the ore bed for a period of 180 h, the pH values of the effluents dropped to about 3. The pH remained slightly lower with the solution that contained CA because of a buffering The flow rates from both columns effect. decreased slightly initially, owing probably to the ore disintegration shown in table 2, but the flow was always greater from the column containing CA because less iron precipitation occurred.

After 85 h of leaching, sodium molybdate was added to both carboys to produce a 10-ppm-Mo solution. The effluent from the column containing the CA solution contained 10 ppm Mo, but none was detected in the column that had no CA. These results further indicate that CA helps to keep molybdenum in solution and also enhances the concentrations of the other ions.

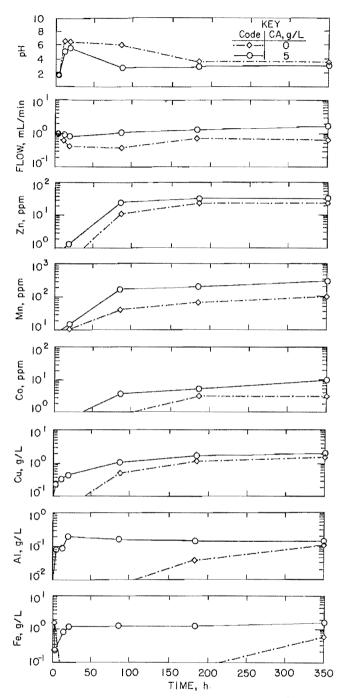


FIGURE 11. - Influence of column leach time and citric acid on solution analyses and percolation flow.

DISCUSSION

In all three phases of the research, ferric ions precipitated from the solutions at a pH of about 3 when chelating reagents were absent. Because most copper ores contain some soluble iron compounds, ferric ions are commonly found in

copper leach solution. The dissolved iron can be in the ferrous or ferric state, but because air is usually readily available, the ferrous is oxidized to the ferric form.

The pH of a conventional copper dump leaching solution is usually less than 3, but higher localized pH values generated by acid-consuming minerals present in the ore can exist within the particles. Acid-producing sulfide minerals may also be present, but this acid may be produced in a different microscopic site and thereby not prevent the iron precipitation in the localized leach cavity.

Experimental results suggest that precipitation of ferric ions can remove other metal ions such as molybdenum. Also iron precipitate may plug voids in the ore bed, which may prevent reactants from reaching metal values in the ore. After the metal values are dissolved, the permeability of the ore bed must be

sufficient to permit the flow of these ions to the liquor recovery operation.

The presence of CA and other chelating reagents appears to have additional advantages besides preventing the precipitation of ferric ion. Other metal ions are also chelated, and this increases their solubility limit. In addition, the test results indicate that CA can be recycled without losing its chelating capability.

The undissolved solids in some of the inexpensive chelating reagents, such as sodium lignin sulfonate, appear to prevent the increased consolidation of the ore particles and aid in the mass transfer of the reactants and the products.

CONCLUSIONS

This report furnishes information on preventing the precipitation of ferric and other ions in copper leach solutions by the use of chelating reagents. The following results were observed.

- 1. The precipitation of ferric compounds removes other metals such as molybdenum from solution.
- 2. The addition of chelating reagent such as 2.5 g/L CA prevents the precipitation of 1 g/L Fe below pH values of 5 if iron is the only metal present. With a simulated copper dump leach solution, 10 g/L CA was sufficient to retain the metal values in solution at pH values below 5.
- 3. Citric acid appears to be more effective in retaining the metal ions in solution at high pH values than does sodium lignin sulfonate, gluconic acid, or oxalic acid.

- 4. Titanium solubility decreases at pH values above 2 even when ferric ions are absent, but with 2.5 g/L CA present, essentially no concentration change was observed at a pH below 5 with or without 1 g/L Fe.
- 5. The presence of CA in the lixiviant decreased the ore bed plugging, and therefore higher fluid flows were obtained.
- 6. At pH values between 3 and 5, the presence of 2.5 g/L CA in the lixiviant enhanced the recovery of aluminum, calcium, cobalt, copper, iron, manganese, molybdenum, titanium, and zinc.
- 7. Decopperizing the copper solution with iron and nickel powder or with LIX 64N did not affect the threshold pH required to precipitate ferric ions in the presence of CA. Thus, CA appears to be recyclable.

REFERENCES

- 1. Bhappu, R. B., P. H. Johnson, J. A. Brierley, and D. H. Reynolds. Theoretical and Practical Studies on Dump Leaching. Trans. SME, AIME, v. 244, Sept. 1969, pp. 307-320.
- 2. Bieniewski, C. L., F. H. Persse, and E. F. Brauch. Availability of Uranium at Various Prices From Resources in the United States. BuMines IC 8501, 1971, 92 pp.
- 3. Brimhall, D. B., and M. E. Wadsworth. Oxygen Consumption in Dump Leaching. AIME Trans., v. 254, Mar. 1973, pp. 68-75.
- 4. Brooke, J. N. Uranium Recovery From Copper Leeaching Operations. Min. Congr. J., v. 63, No. 8, 1977, pp. 38-41.

- 5. Linke, W. F. Solubilities: Inorganic and Metal-Organic Compounds. Van Nostrand, v. 1, 1958, p. 1062.
- 6. Madsen, B. W., and R. D. Groves. Using Oxygen To Reactivate a Nearly Dormant Copper Sulfide Leach. BuMines RI 8056, 1975, 9 pp.
- 7. Leaching Low-Grade Sulfide Ore. Ch. in Extractive Metallurgy of Copper, ed. by J. C. Yannopoulos and J. C. Agarwal. AIME, 1976, p. 939.
- J. C. Agarwal. AIME, 1976, p. 939. 8. Marchant, W. N., S. L. May, W. W. Simpson, J. K. Winter, and H. R. Beard.

- Analytical Chemistry of the Citrate Process for Flue Gas Desulfurization. Bu-Mines IC 8819, 1980, 20 pp.
- 9. Randolph, A. D., R. D. Williams, and D. A. Milligan. Hydrolysis of Iron on a Retained Crystal Bed. Fundamental Aspects of Hydrometallurgical Processes. AIChE Symp., Series 173, v. 74, 1978, pp. 84-96.
- 10. Sheffer, H. W., and L. G. Evans. Copper Leaching Practices in the Western United States. BuMines IC 8341, 1968, 57 pp.